

PERCHLOROETHYLENE EXTRACTION OF SULFUR AND SULFUR COMPOUNDS FROM COAL

David H. Buchanan and Linda C. Warfel

Chemistry Department
Eastern Illinois University
Charleston, IL 61920

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ABSTRACT

Perchloroethylene (PCE) is an excellent solvent for extracting elemental sulfur (S^0) from bituminous coal. The same amount of S^0 is extracted within one hour at reflux (120°C) or 72 hours at 27°C. Extractions at 120°C also remove 1-2 weight % organic material within 30 minutes. Additional heating increases the amount of organic material extracted but decreases the concentration of S^0 in solution due to reactions between sulfur and coal. The elemental sulfur content of ten different mid-western coal samples varies with the sulfatic sulfur content, consistent with the view that both elemental sulfur and sulfate in coal come from weathering of pyrite. The nature of the organosulfur compounds extracted by PCE and by THF has been studied by Sulfur Sensitive Gas Chromatography and GC/MS as described in an accompanying paper by K. Vorres.

INTRODUCTION

Previous studies have shown that hot perchloroethylene (PCE) extracts significant quantities of elemental sulfur (S^0) from several mid-western coals. Narayan reported that 1.6% S^0 by weight was recovered from an Indiana refuse coal and speculated that organic sulfur in coal may in fact exist as insoluble polysulfides which are converted to soluble orthorhombic sulfur (S_8) by hot PCE.(1) S. Lee and H. Lee have reported that ASTM organic sulfur is reduced in the PCE-insoluble product coals after PCE extraction and they have qualitatively identified S^0 in the extracts.(2)(3) However, other studies have shown that little or no S^0 is found in most US coals using other methods.(4)(5)(6) Removal of significant amounts of organic sulfur from coal by simple solvent extraction would be an important contribution to pre-combustion desulfurization.

We have shown that only small amounts of S^0 are extracted by PCE from Illinois coals and that only weathered coals contain extractable S^0 .(7) For at least one coal, pyrite oxidation was shown to be the source of the S^0 extracted.(8) IBC-107 is an Illinois No. 6 coal in which the forms of sulfur have characteristic stable sulfur isotope ratios (SSIR, 34). In this coal, the SSIR for the organic sulfur is 1.9‰, for sulfatic sulfur 13.2‰ and for pyritic sulfur 24.0‰. The elemental sulfur isolated from this coal had an SSIR value of 19.8‰, showing that it was derived from the pyritic rather than the organic fraction of the sulfur in this coal.(8)

Temperature and contact time were found to be important variables for both the reduction of organic sulfur and yield of S^0 by PCE extraction.(1-3)(7) Long term heating of weathered coal with PCE reduces the yield of S^0 .(9) We now report on the effect of temperature on the extraction of S^0 from coals and on the isolation and chromatographic fractionation of organic compounds extracted by PCE. Because early reports on PCE extraction emphasized the isolation of only elemental sulfur, it is important to note that organosulfur compounds are also present in PCE extracts. The identification of organosulfur compounds in these extracts is discussed in the accompanying paper by Vorres.(10)

EXPERIMENTAL PROCEDURES

Coal samples used were Illinois Basin Coal Sample Program (Illinois State Geological Survey - ISGS) IBC-101, -201, -501, and -701; Argonne Premium Coal Sample Program coal No. 3 plus an oxidized version of this coal; an Ohio 5/6 coal from Horizon Coal Co. (C.J. Kulik) and an Indiana Refuse coal (R. Narayan). Unless otherwise noted, all coal samples and solid products were dried to constant weight at 0.1 Torr., 100°C in an Abderhalden apparatus before use or before final weights were determined. Samples were supplied as either -60 or -100 mesh material and were not further reduced in size. Ultimate analyses and ASTM Forms of Sulfur analyses of the actual samples of all feed coals and solid products were performed under the supervision of Dr. Chusak Chaven at the ISGS.

HPLC grade PCE (Aldrich) was fractionally distilled before use to remove traces of a UV-active material which interfered with the UV detector used in the HPLC determination of elemental sulfur. Elemental sulfur for preparation of analytical standards and reactions with coal was sublimed immediately before use to remove traces of amorphous sulfur which did not completely dissolve in PCE.

The Soxhlet extraction method developed for PCE is slightly modified from that reported earlier.(11) A thermometer or thermocouple probe was arranged to measure the temperature inside the extraction thimble in the upper one third of the coal mass. An electric heating tape (Brisket) was wrapped around the glass barrel holding the thimble and the PCE inside was maintained at a slow boil (120°C) during the extraction. Under these conditions, any constriction in the siphon tube of the apparatus interrupted smooth cycling of hot solvent. Solvent was added to the apparatus and brought to temperature and the coal sample added to the solvent in the thimble. At the end of the extraction, the contents of the thimble were vacuum filtered on a 0.45 μ m PTFE membrane filter. In batch extraction experiments, a weighed sample of dry coal was quickly added to a measured volume of well-stirred PCE in a round-bottom flask maintained at a known temperature with an electrically heated oil bath. Product coal was recovered by hot filtration in which the filter funnel and filter paper were heated by boiling PCE vapors from the receiver flask. A thermometer was suspended such that the temperature of the slurry in the filter was measured and maintained above 118°C.

Product coals were recovered by washing with hot 80% methanol/water, filtration and vacuum drying or by steam distilling PCE away from the coal residue. Aliquots of the solvent extracts were analyzed for elemental sulfur by HPLC after passage through a dry-packed Florisil chromatography column (1cm x 30cm) to remove organic compounds which interfere with the analysis. Column flow was adjusted to 1 drop per second and sample eluted with additional pure PCE. The second milliliter to elute from the column was collected for HPLC analysis on a 4.6 x 250 mm C₁₈ reversed phase HPLC column using a mobile phase of 95% methanol/water at 1.5 mL/minute with UV detection at 290 nm. The method was calibrated with standard solutions of sublimed S⁰ in distilled PCE. The calibration samples were also passed through a Florisil clean-up column.

PCE and THF extracts were fractionated for GC/MS studies by published methods.(12)(13) Solvent-free extracts were chromatographed on alumina using hexane, benzene, chloroform and THF/10% ethanol in sequence. PAC fractions (benzene) were re-chromatographed on silica gel impregnated with PdCl₂.

RESULTS AND DISCUSSION

Yields of elemental sulfur extracted are given in Table 1 along with ASTM Forms of Sulfur analyses. A less complete version of this data set has been presented elsewhere.(7)(9) Linear least-squares correlations between weight percent elemental sulfur extracted by PCE and weight percent sulfatic sulfur (ASTM) are

shown below the data. Since S^0 is both produced and consumed during pyrite oxidation, the numerical value of the relationship is probably not a simple ratio of reaction rate constants. The significance of the data is that S^0 is only found in weathered coals, and then in amounts proportional to sulfatic sulfur which is widely conceded to arise from pyrite oxidation. These results, taken with the stable sulfur isotope ratio study, (8) make a strong case for pyrite oxidation as the only source of S^0 necessary to explain PCE extractions.

The reduction in ASTM organic sulfur in the product coals (PCE-insoluble residues) ranged from 2 to 24% by weight. Total sulfur material balances (product coal, PCE extract and wash solvent, if any) ranged from 87 to 102%, with most values from 92 to 96% by weight, Table 2. To date, only coal 0560 has given an organic sulfur reduction above 11%. Because of the many errors in ASTM organic sulfur values, it is important to determine how all of the sulfur in the feed coal is distributed among the product fractions and not just report an apparent loss of sulfur from one fraction.

Our preliminary studies (7) and others (2)(3) have shown that extractions at 90-110°C recover less S^0 than those in which the temperature is carefully maintained at 120°C, the boiling point of PCE. Additional heating at 90 - 115°C decreases rather than increases the yield of S^0 extracted. The studies summarized in Figures 1 and 2 show this behavior to derive from two competing processes - rapid solution of S^0 by processes proceeding even at 27°C, and retrograde reactions between sulfur and coal which occur only at the higher temperature.

Figure 1 shows that the same yield of S^0 is obtained from IBC-101 coal in a batch extraction after 72 hours at 27°C as was obtained under optimum Soxhlet extraction conditions, 3 hours at 120°C. At 120°C, the maximum yields in batch extractions occur at one half hour. Figure 2 shows the decrease in concentration of S^0 remaining in solution when approximately 12 g of APCSP No. 3 coal or a heavily oxidized fraction of that coal (E0935, Table 1) was heated with 1.7 millimoles of elemental sulfur in 150 mL of PCE at 120°C for 816 hours under nitrogen. A control experiment minus the coal did not lose appreciable amounts of sulfur during that time. The initial increase in S^0 concentration for E0935 is due to solution of the S^0 originally present. A plot of $\ln[S^0/S^0_{int}]$ vs time for the premium coal was linear through four half lives and gave an apparent first-order rate constant of $9.7 \times 10^{-7} \text{ sec.}^{-1}$ for the disappearance of sulfur.

Conditions which maximize the yield of S^0 do not maximize the yield of organic compounds also extractable from coal. PCE extracts 1-2% by weight organic material from coals. The solvent-free extracts have elemental compositions similar to toluene extracts of the same coals, (11) as expected for a non-polar, non-swelling solvent. We measured the volumetric swelling ratio of IBC-105 coal in PCE to be 1.03 at 25° and 1.06 at 90°C. The total sulfur content of the PCE extract of IBC-105 is 2.1%, essentially the same as the ASTM organic sulfur content of the feed coal. Sulfur contents of PCE extracts of weathered coals are greater than that value by the amount of elemental sulfur extracted. In order to characterize organosulfur compounds removed by PCE, several extracts were fractionated on alumina (12) and on Pd impregnated silica gel. (13) Typical recoveries of fractionated extracts for both PCE (non-polar) and THF (polar) are shown in Table 3. Recovery data show that considerable polar material, especially from the THF extract, remains bound to the column. Stripping the column with pyridine followed by methanol did not raise the total recoveries above 73% for PCE extracts or 40% for THF extracts. Elemental sulfur, when present, elutes with the AHC fraction, in which it was detected by both HPLC and GC/MS. Both fractionated and un-fractionated extracts were analyzed by Sulfur Sensitive Gas Chromatography and Gas Chromatography/Mass Spectrometry at Argonne National Laboratory. The results of that study are discussed in the following paper. (10) The organosulfur compounds identified to date are typical of those

reported by others for non-polar extracts of bituminous coals.(13)(14)

CONCLUSIONS

PCE is an excellent solvent for the extraction of elemental sulfur from coals in that the process is quickly completed and very little organic material is lost from the feed coal to the solvent. However, only weathered coals contain elemental sulfur which is the result of pyrite oxidation. PCE extraction does not remove more than 10% true organic sulfur from most coals. Elemental sulfur dissolved in PCE reacts with coal at 120°C to become bound to the coal an effect which may explain why exhaustive extractions with other solvents have failed to yield elemental sulfur.

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Table 1

ASTM FORMS OF SULFUR AND S° EXTRACTED BY PCE FOR WEATHERED COALS

EIU #	Sample Bank #	% S° by PCE	% Total S	% Sulfatic ASTM	% Pyritic ASTM	% Org S (Diff)
HERRIN SEAM ILLINOIS No. 6						
0930	APCSP-3	0.000	4.83	0.010	2.47	2.35
0630	IBC-105	0.0006	4.24	0.010	2.60	1.63
0620	IBC-105	0.037	4.46	0.373	2.26	1.83
0650	IBC-105	0.1085	4.31	0.77	1.45	2.17
E0935	APCSP-3	0.127	4.67	0.934	1.83	1.91
OTHER ILLINOIS/INDIANA COALS						
0300	IBC-101	0.034	4.23	0.127	1.40	2.70
0410	IBC-102	0.199	3.22	0.466	1.88	0.87
0710	IBC-107	0.032	3.77	0.272	0.71	2.79
RN20	INDREFUSE	1.54	11.7	5.96	4.46	1.28
0560	OHIO 5/6	0.058	3.44	0.381	1.18	1.83

ALL 10 SAMPLES: $\% S^{\circ} = 0.260 * [\% \text{ Sulfatic S}] - 0.028$ $r^2 = 0.993$

HERRIN SEAM: $\% S^{\circ} = 0.140 * [\% \text{ Sulfatic S}] - 0.0048$ $r^2 = 0.994$

Table 2

DECREASE OF ORGANIC SULFUR IN PRODUCT COALS AND TOTAL SULFUR MASS BALANCE

Sample Number	Wt% PCE Extract	Wt% Coal Product	Wt% Organic Sulfur in Product	% OS Lost	Mass Balance Sulfur
0410	1.57 %	97.5 %	0.88 %	1.34 %	93.3 %
0560	1.70	98.8	1.44	24.00	97.7
0620	1.77	99.8	1.70	7.28	91.2
0630	1.64	97.3	1.53	8.70	95.2

FRACTIONATION SCHEME

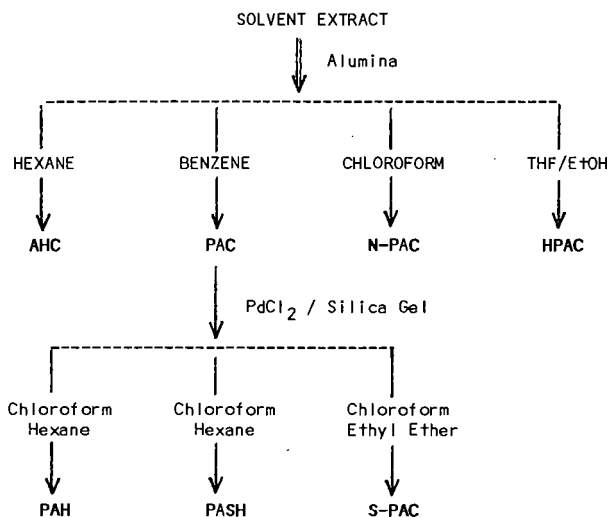


Table 3

FRACTIONATION OF PCE AND THF EXTRACTS

Sample Number	Extract Solvent	Wt % of Extract in Alumina Column Fractions			
		AHC	PAC	N-PAC	HPAH
0560	PCE	20.90 %	22.15 %	16.82 %	8.20 %
0630	PCE	7.24	14.79	15.73	21.54
0930	PCE	8.87	17.28	15.41	28.28
0630	THF	1.44	4.47	3.54	27.88
0930	THF	3.17	3.80	5.06	15.75
		Wt % of PAC in Silica Gel Column Fractions			
		PAH	PASH	S-PAC	
0630	THF	79.69	15.66	14.97	

Wt % S Extracted vs Time

Effect of Temperature

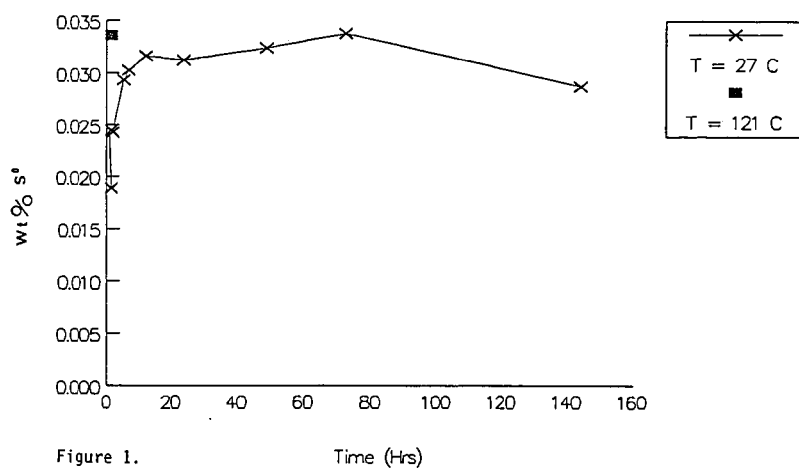


Figure 1.

[Sulfur] in PCE vs Time

T = 120°C

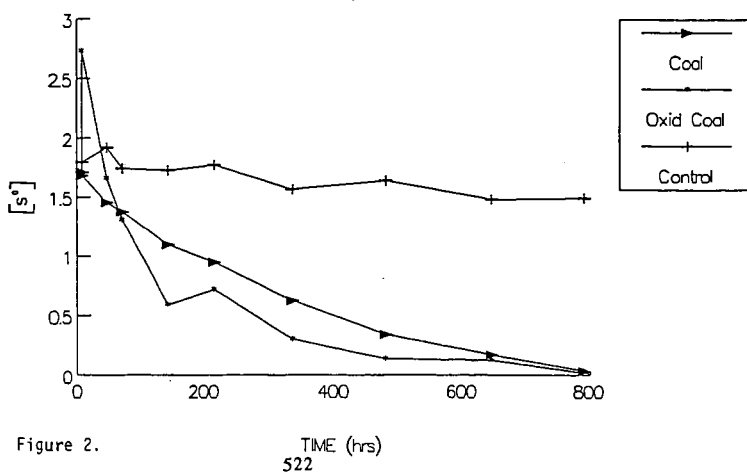


Figure 2.